X-RAY DIFFRACTION STUDY OF COPPER AT HIGH TEMPERATURES

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ABSTRACT. Spectroscopically pure copper was cold worked upon by drawing it in form of a wire and was annealed at 500°C for about eight hours when equilibrium conditions were achieved. X ray diffraction photographs of the sample at various high temperatures were taken The lattice parameters as obtained from the photographs gave a nonlinear plot against temperature The plot of the reciprocal of the volume expansion against the reciprocal of the product of the absolute temperature and the Debye function for energy at that temperature was found to be nonlinear. Similar results have been obtained by analysing the data due to Nix and Mac Nair. An exponential form of Grunoisen equation has been shown to explain all the above results

INTRODUCTION

The lattice parameter of pure copper at room temperature has been determined by various authors. A very accurate determination on an extremely pure sample of copper has been carried out by Hume Rothery and Andrews (1942). Before them, Esser, Eilander and Bungardt (1938) also determined the same value and claimed great precision in their measurements, Both these groups of workers arrived at the same value, viz., 3.6074 A.U. at 18°C. These workers had also determined the lattice parameter at various high temperatures. Recently, Eppelsheimer and Penman (1950) have made the same measurements. The values obtained by these various groups of investigators were found to differ from one another. Miller and Russel (1952, 1953) and Eshelby (1953) have shown that lattice defect cause differences in thermal expansion It is difficult to decide whether this difference is to be attributed to the difference in purity of the samples studied or to the states of strain in them. It was therefore decided to measure the lattice parameters of a sample of copper of known purity and an estimated amount of residual strain

II. EXPERIMENTAL

(a) *Description of the sample*

A spectroscopically pure rod of copper supplied by M/s. Johnson Mathey and Co. Ltd , London, was used for preparing the sample. Spectroscopic exami-

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nation revealed that it contained an estmated amount of 3 in a million of nickel and lead, of 1 in a million of silicon, iron and lithium, of 0.5 in a million of silver and manganese and less than 1 in a million of sodium, potassium, magnesium and calcium. The copper rod was drawn into a thin wire about 0.5 mm in diameter with the help of a jeweller's die. The cold working consisted of drawing as well as hammering previous to drawing. The sample was then maintained at 500°C for 12 hours and annealed so that room temperature (30°C) was reached after 12 hours. This process was repeated several times till the lattice spacings at 30°C became constant. This indicated that equilibrium conditions were attained. An idea of the defect introduced by cold working was obtained by measuring the resistivity of the sample at room temperature. The specific resistivity of this sample of copper was found to be 1.61×10^{-6} ohms/c.c. as against 1.5106×10^{-6} ohms/c.c. for a single crystal of copper (Metals Handbook).

(*b*) *X-ray diffraction Technique.*

For determining the lattice parameters of cold worked copper at various temperatures, X-ray powder diffraction technique was used. Nickel filtered copper radiations were used to irradiate the sample mounted on the axis of a 19 cm high-temperature camera. The sample was mounted very carefully on the axis of the camera so as to eliminate the slightest eccentricity. The absence of eccentricity was confirmed by examining the sample through a powerful microscope while the sample was being rotated. The sample was so adjusted that it was found stationary during the rotation for vertical as well as horizontal mount of the microscope. The temperature of the sample was maintained constant with the help of a thermostatic arrangement within ± 1°C.

The diffraction pattern was calibrated against the powder diffraction pattern of quartz taken with the same camera and under identical experimental conditions. For determining the values of the lattice parameter accurately the well known extrapolation technique developed by Sinclair and Taylor (1945) and by Nelson and Riley (1945) was adopted. For each observed value of the lattice spacing '*d*' the corresponding value of the edge length of the cubic cell '*a*' was calculated and plotted against

$$f(\theta) = \frac{\cos^2\theta}{\sin\theta} + \frac{\cos^2\theta}{\theta} \qquad \ldots \quad (1)$$

where θ is the Bragg angle. The extrapolated value of '*a*' for $f(\theta) = 0$ was accepted to be the true value of the lattice parameter. The accuracy obtained in the measurement of *a*' was estimated to be ± .0001 A.U.

III RESULTS AND DISCUSSIONS

(a) *Thermal Expansion*

The lattice parameter of copper for various temperatures ranging from 27°C to 527°C are tabulated in Table 1. The change of the lattice parameter with

temperature is shown graphically in Fig. 1. The plot thus obtained is non-linear showing that the rate of change of lattice parameter is not constant. The values of da/dT for different temperatures have been determined from the experimental curve shown in Fig. 1 These have been tabulated in Table II. The experimental results shown in Tables I and II can be summarised by the equation

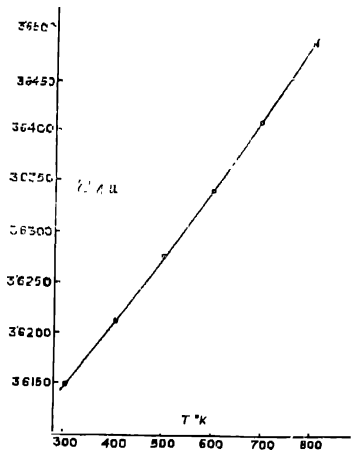

Fig 1. Lattice dimensions of copper at different temperatures.

$$a_T = 3\ 61293 + 5.81\times10^{-5}T + 3.7\times10^{-8}T^2 - 5.2\times10^{-11}T^3 \qquad (2)$$

where a_T is the lattice constant of copper sample at the temperature T°K.

TABLE I

The variation of lattice constant of copper with temperature (obtained from the present investigation).

Temp. °K	a' A.U.
303	3.6147
403	3 6210
503	3.6276
603	3.6342
703	3.6412
803	3.6486

TABLE II

The values of (da/dT) and the coefficient of linear thermal expansion for copper at different temperatures obtained during present investigation

Temp. °K	$(da/dT) \times 10^5$ A.U /°K	Coeff of linear thermal expansio $\times 10^6$
300	6.0	16 60
400	6 2	17.12
500	6 6	18 19
600	6.8	18.71
700	7 2	19 78
750	7.4	20 30

Values of 'a' for copper have been obtained by Hume Rothery and Andrews (1942) at 291°K. 573°K and 773K° respectively. The difference between the values obtained by these authors and the authors of the present investigations may well be due to the changes caused by lattice defects. Vegard and Kloster (1934) reported to have obtained the cell dimensions of copper at 748°K as 3.6589A.U. Nix and MacNair (1942) have also measured the fractional changes in length of copper at various temperatures with respect to its length at 273°K. Their results have been converted into data for lattice parameter at various temperatures with the help of present measurements. Nix and MacNair (1942) have carried out their measurements on a massive polycrystalline annealed sample of copper. Their sample may be taken to be more or less strain free. It is apparent that the lattice dimensions, according to Nix and MacNair (1942) were always less than those of the sample of copper under study. This may very well be attributed to the difference in lattice defect in the two samples due to different residual strains.

Eppelshimer and Penman (1950) have shown that there is no anisotropy in the thermal expansion of copper. A study of the thermal expansion in the various directions of the cold worked copper did not reveal any anisotropy. However, for greater concentration of defects some anisotropy of thermal expansion may be expected.

The thermal expansion of solids has been attributed to the anharmonic vibration of atoms about their mean position. If the potential energy of the atom at a displacement x from their equilibrium separation at 0°K be expressed as

$$U(x) = ax^2 - bx^3 - cx^4$$

where the terms in x^3 represent the asymmetry of the mutual repulsion of the

atoms and the x^4 terms the general 'softening' of the vibration at large amplitudes, the average desplacement at temperature $T°K$ can be shown to be (Kittel, 1954).

$$\bar{x} = 3kTb/4a^2$$

where k is the Boltzmann constant. Thus the coefficient of thermal expansion $(1/x_0)\ dx/dT$ is expected to be independent of temperature. However, as the present experiment reveals, the coefficient of thermal expansion is dependent on temperature. This dependence has been attributed to various types of lattice defects.

(b) *The Gruneisen equation*

Gruneisen (1910) established the relationship connecting the volume expansion $(\partial V/\partial T)$ of a solid with its atomic specific heat C_v given by

$$\left(\frac{\partial V}{\partial T}\right)_p = \gamma K_0 C_v \qquad \ldots (3)$$

$$\left(\frac{1}{V_0}\right)\frac{\partial V}{\partial T} = \frac{\gamma K_0}{V_0} C_v$$

$$3\alpha = \frac{C_v}{Q} \qquad \ldots (4)$$

where Q represents the expression $V_0/\gamma K_0$ where V_0 is the volume of the solid at absolute zero and K_0 is the compressibility at the same temperature. γ is a constant known as Gruneisen constant and α is the coefficient of linear expansion. α is thus proportional to C_v and the variation of α with temperature should be of the same nature as that of C_v.

The above relationship due to Gruneisen can be expressed in various ways Hume Rothery (1945) has discussed the various forms and has recommended the one due to Simon and Vohsen (1928) which states that

$$\frac{V_T - V_0}{V_0} = \frac{E_T}{Q - KE_T} \qquad \ldots (5)$$

where V_T and V_0 are volumes of the solid at T°K and 0°K respectively, E_T the energy imparted to the solid during the change in temperature and Q and K are constants of the substance under investigation. Q in Eq. (5) is identical with that in Eqn. (4). From Eqn. (5), we have

$$\frac{V_0}{V_T - V_0} = \frac{Q}{E_T} - K \qquad \ldots (6)$$

Putting the Debye expression $9RTD(\theta/T)$ for the energy at $T°K$, where R is the

universal gas constant, $D(\theta/T)$ represent the Debye function for energy θ being the characteristic temperature. We may write

$$\frac{V_0}{V_T - V_0} = \frac{Q}{9RT.D(\theta/T)} - K$$

or

$$\frac{1}{3} \cdot \frac{a_0}{a_T - a_0} = \frac{Q}{9RT.D(\theta/T)} - K \qquad \ldots (7)$$

Eqn. (7) clearly shows that the plot of $a_0/a_T - a_0$ against $1/T.D(\theta/T)$ should be a straight line. In fact, Fischmeister (1956) actually obtained straight lines representing the variation of $a_0/a_T - a_0$ with $1/T.D(\theta/T)$ for alkali halides. In the present investigations the method used by Fischmeister (1956) for determining the $a_0/(a_T - a_0)$ was adopted. We know

$$(a_T - a_0)/a_0 = (a_T - a_r)/a_r \left(\frac{a_r - a_0}{a_0} + 1 \right) + \frac{a_r - a_0}{a_0}$$

where a_r represent the lattice constant at the room temperature T_r. Also from Eqns. (4) and (5) with approximation

$$(a_r - a_0)/a_0 = \frac{E_r}{3Q} = \frac{\alpha E_r}{C_v} \qquad \ldots (8)$$

where E_r is the energy of the solid at room temperature and C_v is the atomic heat at the same temperature a_T, a_r and α are the experimentally determined quantities E_r and C_v were calculated from appropriate Debye expressions and thus $(a_T - a_0)/a_0$ was obtained.

The plot of $a_0/a_T - a_0$ vs $1/T.D(\theta/T)$ is shown in Fig. 2A. It is found to be nonlinear, more or less parabolic, in contradiction to what is expected.

The nonlinearity of the above plot can be attributed to one or more of the following reasons :

(1) Change in the Debye characteristic temperature due to cold working.

(2) limitations of the Debye approximation in deriving the expression for energy E_r.

(3) inaccurate value of α obtained by the extrapolation embodied in Eqn. (7).

(4) variation with temperature of γ the Gruneisen constant resulting in change of Q with temperature.

Non-linearity in the $a_0/(a_T - a_0)$ vs $1/T.D(\theta/T)$ curves for a number of cubic face centered metals has recently been observed by Mitra and Mitra (1957). In

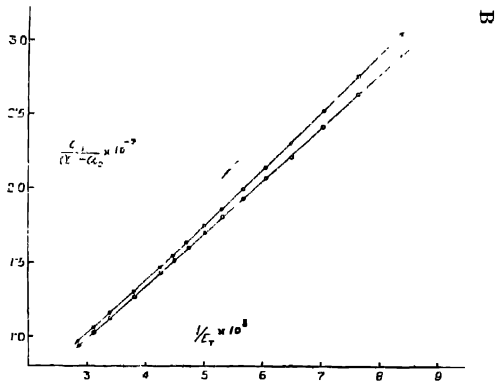

Fig. 2. Plot of $\frac{a_0}{a_T - a_0}$ against $\frac{1}{E_T}$ for copper.

a_0 = lattic constant of copper at O°K.

a_T = " " " " " T°K.

$E_T = \int_0^T C_v dT$.

C_v = atomic heat of copper at constant volume.

A—E_T calculated from Debye formula.

B—E_T calculated from experimentally obtained values of C_v.

order to eliminate uncertainties due to (2) and (3), $E_T = \int_0^T C_v \, dT$ can be determined from purely experimental values and a_0 can be obtained by extrapolation of a_T vs T curve at very low temperature region.

(c) *Extrapolation of a*

For the above purpose, it has been found convenient to analyse the data due to Nix and MacNair (1941). Their data have been acclaimed to be extremely accurate and cover a very wide range from 80°K to 800°K. Moreover, the data are for noncoldworked specimen of pure poly-crystalline copper. So the existing specific heat data will be applicable to it Nix and MacNair (1941) have tabulated the values of $\Delta l/l$ the fractional change in length with temperature, l being the length at 0°C. In order to convert the data due to Nix and MacNair (1941) to that suitable for drawing the a vs T curve, the value of a at 30°C has been taken to be 3.6147A.U., the value obtained by the present authors. $\Delta a/a_0 = 5.047 \times 10^{-4}$ according to Nix and MacNair (1941). From this a at 0°C has been found to be 3.6129 A.U. Values of a at various temperatures have been determined in a similar way and have been plotted against respective temperatures. This curve is shown in Fig. 3. It will be seen that the curve shows an almost

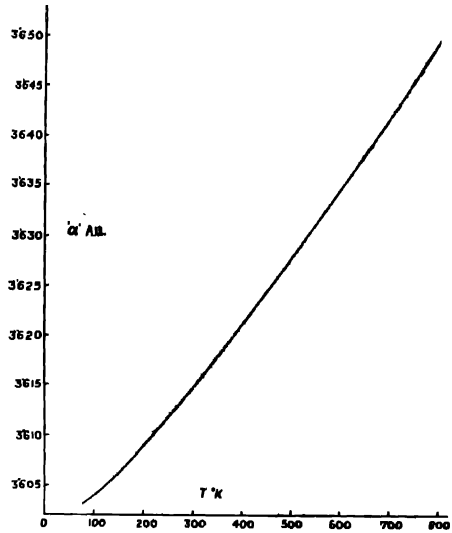

Fig. 3. Plot of lattice constants of copper at different temperatures. Data due to NiX and Macvair (1941).

linear declination with fall in temperature but shows a sharp bend after 150°K. The curve in the region 80°K to 100°K can be fitted with the equation.

$$a_T = 3.60305 - 1.75 \times 10^{-5} T + 2.6 \times 10^{-7} T^2 \qquad \ldots \quad (9)$$

from the above equation, the value of a at absolute zero has been found to be 3.60305.

(d) *Evaluation of* E_T

For the evaluation of $E_T = \int_0^T C_v dT$, values of C_p at various temperatures tabulated by Furukawa and Douglas (1957) were plotted against corresponding temperatures. From this plot required values of C_p have been determined. Values of C_v at various temperatures have been calculated from the thermodynamic relationship.

$$C_p - C_v = \frac{9\alpha_T^2 . K_T . T}{J\rho_T} \qquad (10)$$

where α_T is the coefficient of linear expansion at T°K.
K_T is the bulk modulus at T°K.
ρ_T is the density at T°K.
and J is the mechanical equivalent of heat

$\frac{1}{a_0}\left(\frac{da}{dT}\right)_T$ was calculated from the graph in Fig. 3 and with the extrapolated value of a_0. K_T was taken from the date of Overton and Gaffney (1955). ρ_T was calculated from the experimentally obtained values of α_T and from space group considerations. The values of C_v at various temperatures thus obtained were plotted against the corresponding temperature and the area of the plot enclosed between 0°K to T°K gave the value of $\int_0^T C_v dT = E_T$ at T°K.

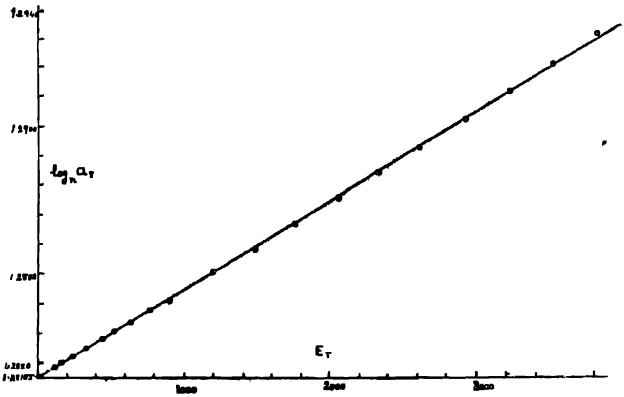

Fig 4. Plot of logarithm of a_T against E_T. For explanation of symbols see caption of Fig, 2B

With values of a_T, a_0 and E_T thus obtained $a_0/a_T - a_0$ was plotted against $1/E_T$ for various values of T. The resultant curve is shown in Fig. 2B. This is non-linear although with lesser curvature than Fig. 2A.

(e) log a_T—E_T curves.

In this connection, it is interesting to note that the plot of $\log_e a_T$ against E_T as shown in Fig. 5 is linear. The intersection of this straight line with the axis of $E_T = 0$ yields the value of log, a_0 from which a_0 is found to be 3.6024A.U. The plot of $a_0/(a_T - a_0)$ against $1/E_T$ from this value of a_0 is observed to be very nearly linear in agreement with the Gruneisen equation. It thus appears to

be evident that the non-linearity in Fig. 3A and Fig. 2B were due to inaccurate values of a_0. The correct value of a_0 is obtained from the plot in Fig. 4 which suggests the equation.

$$a_T = a_0 e^{CeT} \qquad \ldots \quad (11)$$

C being a constant. C has been calculated from the slope of the straight line in Fig. 4 and is found to be identical with $1/3Q$ where Q 120×10 cal/mol. It is the same value as used by Nix and MacNair (1941) to fit their result with Eqn. (6). Thus from Eqn. (10). we can write

$$a_T = a_0 e^{E_T/Q}$$

$$= a_0 \left(1 + \frac{E_T}{3Q} \right) \text{terms involving higher powers of } E_T/3Q.$$

$$= a_0 (1 + E_T/3Q) \text{ where } E_T/3Q \text{ is small.}$$

$$= 3Q/E_T \qquad (12)$$

which is the same as Eqn. (6) but for the correction term K can be taken care of by modifying Eq. (11) into $a_T = a_0\, e^{KE_T/3(Q-kE_T)}$ which reduces to Simon and Vohsen form of Gruneisen equation in the first approximation provided that it thus appears that the correct relationship between a_T and E_T is given by Eq. (13) which reduces to Gruneisen relationship in the first approximation. It is possible that the slight departure from Gruneisen relationship shown by most metals is natural consequence of equation (13) and need not be corrected by assuming fictitious values of either the Debye characteristic temperature as suggested by Nix and MacNair (1941) or for Q as suggested by Hume Rothery (1945). However, Eqn. (12) should be tested at very low temperatures to ascertain whether the value of a_0 obtained from it is correct. We are carrying on investigations on other metals and alloys to find out whether Eqn. (12) holds good fo them too.

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